

PATENT APPLICATION

OF

MICHAEL STANLEY DeCOURCY,

LESLI BERNADETTE POOLE

AND

PATRICK KEVIN PUGH

FOR

**METHOD FOR REDUCING WASTE OXIDE GAS EMISSIONS IN
INDUSTRIAL PROCESSES**

DN A01465

U.S. POSTAL EXPRESS MAIL LABEL NO. EU416302486US

METHOD FOR REDUCING WASTE OXIDE GAS EMISSIONS IN INDUSTRIAL PROCESSES

FIELD OF THE INVENTION

This invention relates to methods for reducing unwanted emissions in industrial processes. More specifically, this invention relates to methods for decreasing the production of waste oxide gases during thermal oxidation.

BACKGROUND

Thermal oxidizers are often utilized to dispose of waste streams from industrial processes. In a typical thermal oxidizer, a waste stream and an oxidant are combined at high temperature in order to decompose the waste. If the waste stream is well mixed with the oxidant, and the waste is maintained at high temperature within the thermal oxidizer for a sufficient time period, waste destruction will occur through a combination of oxidation reactions. Often, it is also necessary to provide a fuel stream to the thermal oxidizer. The fuel stream is concurrently combusted in the thermal oxidizer to maintain the desired waste destruction temperature. In some instances, waste heat recovery equipment, such as a heat recovery steam boiler (HRSB), may also be incorporated into the thermal oxidizer, but this is not the primary aim. For thermal oxidizers, it is necessary to maximize waste destruction efficiency first and foremost and the utilization of a HRSB is purely optional.

Because of the high temperatures required to maintain destruction efficiency (typically 600° C or higher), waste oxide gases ("WOG") are often

produced as a byproduct of thermal oxidizer operation. Waste oxide gases are those gases containing nitrogen based oxides (NO_x), sulfur-based oxides (SO_x), carbon-based oxides (CO_x), or combinations thereof. Such waste oxide gases are produced by a variety of processes including chemical, combustion, or thermal processes.

When introduced to the environment, waste oxide gases can produce undesirable effects. For example, nitrogen based oxides play a major role in the formation of ozone and believed to be responsible for the nitric acid component of acid rain. Sulfur-based oxides are associated with acidification of lakes and streams, accelerated corrosion of buildings and monuments, reduced visibility and adverse health effects. Carbon-based oxides, most notably carbon monoxide, may present serious health concerns to the public and have been linked to global warming. Due to these serious adverse environmental and health effects, introduction of waste oxide gases to the environment is strictly regulated by both national and regional agencies. Such regulations are expected to become even more restrictive in the coming years.

One objective of a thermal oxidizer is to destroy waste compounds, preferentially converting them into innocuous carbon dioxide and water. Thus the aforementioned generation of WOG is an undesirable effect which industry would prefer to minimize. While many different designs and configurations for thermal oxidizers have been proposed, all comprise at least

one high temperature waste destruction zone and therefore produce at least some WOG.

In contrast to thermal oxidizers, industrial boilers convert the heat from fuel-combustion into steam. Industrial boilers (also referred to as utility boilers, commercial boilers, institutional boilers, or direct fired boilers) comprise at least one combustion zone (generally referred to as the “furnace” section) and at least one steam boiler section. The steam produced from an industrial boiler may be used for heating applications – such as the operation of distillation columns in refineries – or more typically, the steam is used to provide the motive force for steam turbines drives coupled to electric power generators. Despite this difference in objective, industrial boilers also produce WOG as a result of their operation.

Because there are many more industrial boilers in use than thermal oxidizers, the majority of WOG emissions-reduction work to date has been focused on improving industrial boiler rather than thermal oxidizer operations. In particular, the United States Government, as well as many industrial boiler manufacturers, has directed significant research effort toward the reduction of NO_x emissions produced by industrial boilers. The emission reduction methods developed as a result of this work take advantage of the fact that industrial boilers utilize a limited number of fuels – primarily coal and high purity natural gas – and that these fuels have relatively constant compositions and are used at essentially constant firing rates.

It has been proposed that some of the known industrial boiler emission reduction methods may also be applicable to industrial process thermal oxidizers. Unfortunately these methods are of only limited utility. All industrial boiler emission reduction methods involve substantial capital, operating, or maintenance costs. Which makes these methods economically unattractive when applied to waste destruction systems. Moreover, blind application of boiler-related methods to industrial thermal oxidizers may result in reduced waste destruction efficiency and frequently generates by-products that are as detrimental to the environment as the waste oxide gases themselves.

Traditional waste oxide gas reduction methods for industrial boilers can be grouped into two broad categories: combustion modifications and post-combustion processes. The reduction methods that inhibit the formation of NO_x are referred to as “combustion modifications” and include low NO_x burners, overfire air, reburning, flue gas recirculation, and operational modifications. The reduction methods that destroy NO_x once formed are referred to as “post combustion processes.” The post combustion processes include Selective Catalytic Reduction, Selective Non-Catalytic Reduction, and hybrid processes.

Low NO_x burners (LNBs) are one combustion modification method designed to control the mixing of fuel and air to achieve what amounts to a staged combustion. Staged combustion involves some combustion in a primary stage and additional combustion in a reburn stage portion of the

waste destruction device. Consequently staged reduction reduces both flame temperature and oxygen concentration during some phases of combustion, which in turn reduces both thermal NO_x and fuel NO_x production. To accomplish staged combustion fuel gas, in addition to the fuel gas delivered to the primary combustion stage, is required to be provided to the reburn stage. The potential advantage of this practice is countered by the consumption of excess fuel gas in the reburn portion of the device.

Changing certain boiler operational parameters can create conditions in the furnace that will lower NO_x production – such changes are generally referred to as Operational Modification Methods. Examples include burners-out-of-service (BOOS), low excess air (LEA), and biased firing (BF).

Conventional combustion modification methods, such as those described above, are either very capital intensive or, in the case of operational modifications, detrimental to achieving the required waste destruction efficiencies. As previously mentioned, methods that destroy NO_x once formed are referred to as “post combustion processes” and include Selective Catalytic Reduction (SCR), Selective Non-Catalytic Reduction (SNCR), and hybrid processes.

It should be noted that, while conventional post combustion methods are able to achieve some level of reduction in WOG emissions, they are not without undesirable environmental drawbacks. For instance, use of SNCR leads to release of ammonia and nitrous oxide into the environment. Released ammonia can lead to adverse impacts downstream of the SNCR system,

including air heater fouling, plume formation, and contamination of otherwise noticeable fly ash. SCR can also have undesirable effects, such as the release of ammonia, enhanced production of undesirable sulfur oxides and high gas-side pressure drops. Moreover, ammonia handling and storage, necessitated by SNCR and SCR methods, presents serious safety concerns. Furthermore, the SCR abatement method employs zeolite or precious metal catalysts. Such catalysts are not only expensive to purchase but costly to dispose of when their useful life has ended. The catalysts are also sensitive to contaminants, such as sulfur-containing compounds, and the system can readily foul (*e.g.*, in-situ formation of ammonium sulfate). Maintenance costs are also increased with oxide destroying methods and specialized continuous emissions monitoring equipment is often required to monitor the performance of the system.

Accordingly many drawbacks exist with current industrial methods of reducing waste oxide gases associated with thermal oxidizers. As such, a need exists for a simple, low capital, high efficiency process where thermal oxidizers within industrial processes could be operated with minimal waste oxide gas emissions and while maintaining optimal destruction efficiency during waste destruction. Further, a need exists for a thermal oxidizer capable of producing a reduced amount of waste oxide gases without requiring the need for fuel gas downstream of the primary combustion zone.

STATEMENT OF INVENTION

Therefore, one embodiment of the present invention provides novel methods for reducing waste gas oxide emissions in industrial processes. Another embodiment of this invention provides novel waste destruction processes that produce lower waste gas oxide emissions. These and other novel features will be apparent to those skilled in the art after reading the specification and appended claims.

Accordingly, one embodiment of the present invention provides novel processes for reducing the generation of NO_x emissions. These processes comprise the steps of: directing a waste stream to a thermal oxidizer; combusting at least a portion of the waste stream in the primary combustion zone of the thermal oxidizer; and injecting at least a portion of the waste stream in the downstream waste destruction zone of the thermal oxidizer. The waste stream comprises approximately at least 0.5 mole% of reactive waste components and up to approximately 99.5 mole% of inert components. It is preferred that the waste stream comprises approximately at least 2.0 mole% of reactive waste components and up to approximately 98 mole% of inert components.

The method of the present invention further comprises supplying an aqueous waste stream to the primary combustion zone. Also included in the present invention is the step of supplying ancillary waste to the downstream waste destruction zone wherein the ancillary waste is selected from the group consisting of aqueous waste and alternative waste.

The method of the present invention can be combined with an industrial process where product produced by the industrial process is selected from the group consisting of acrylic acid, methacrylic acid, acrolein, methacrolein, hydrogen cyanide, acrylonitrile, methacrylonitrile, phthalic anhydride, maleic anhydride and mixtures thereof.

An alternative embodiment of the present invention involves a method for reducing the emission of waste oxide gas of an industrial chemical process where the industrial chemical process produces products selected from the group consisting of: methacrylic acid, acrolein, methacrolein, hydrogen cyanide, acrylonitrile, methacrylonitrile, phthalic anhydride, maleic anhydride, and mixtures thereof. The alternative embodiment of the present invention comprises the steps of directing a waste stream to a horizontal thermal oxidizer; combusting at least a portion of the waste stream in the primary combustion zone of the thermal oxidizer; and injecting at least a portion of the waste stream in the downstream waste destruction zone of the thermal oxidizer. The waste stream of the alternative embodiment comprises approximately at least 0.5 mole% of reactive waste components and approximately up to 99.5 mole% of inert components. The alternative embodiment of the present invention also comprises supplying an aqueous waste stream to the primary combustion zone. The alternative embodiment of the present invention also comprises supplying ancillary waste to the downstream waste destruction zone wherein the ancillary waste is selected from the group consisting of aqueous waste and alternative waste.

Figure 1 illustrates a schematic of one embodiment of the present invention as it applies to a horizontal multistage thermal oxidizer.

Figure 2 depicts a schematic of an alternative embodiment of the present invention as it applies to a vertical multistage thermal oxidizer.

DETAILED DESCRIPTION

The present invention relates to methods for reducing waste oxide gas emissions. Specifically, waste oxide gas emissions produced within a thermal oxidizer can be reduced by the use of a multi-zone waste thermal oxidizer comprising at least one primary combustion zone and at least one downstream waste destruction zone. By performing the primary combustion of fuel prior to the destruction of at least a portion of the waste, it has been discovered that waste oxide gas emissions from the waste destruction process can be reduced economically and without significant loss of overall waste destruction efficiency. It has further been discovered that the addition of aqueous waste streams to the primary combustion zone can also work to reduce waste oxide gas emissions.

With reference to the drawing herein, a method for reducing waste oxide gas content in emissions according to one embodiment of the present invention is shown in Figure 1. Like numbers represent like streams, steps, and elements. The thermal oxidizer 20 of Figure 1 is shown in a schematic representation as a multistage horizontal thermal oxidizer. In the embodiment of Figure 1, an oxidant stream 10 is combusted with a combustion fuel stream 12 within the primary combustion zone 22 of the thermal oxidizer 20. The oxidant stream 10 contains one or more gases and comprises from 1 to 100% oxygen. Examples of suitable oxidants include but are not limited to atmospheric air, pure 100% oxygen, oxygen-enriched air, ozone, or oxygen-containing process vent gases. In some embodiments,

rather than providing a mixed oxidant stream, its may be advantageous to utilize two independent oxidant streams which are introduced into the thermal oxidizer separately but within sufficiently close proximity to promote good mixing once inside the thermal oxidizer. For example, for safety and operability reasons, an atmospheric air stream may be injected via a nozzle separate from, but in close proximity to, a pure-oxygen addition lance.

As shown in Figure 1, a portion of the oxidant stream 10 may also be optionally diverted at a tee 11, to provide the supplemental oxidant stream 13. Injecting the supplemental oxidant stream 13 into one or more of the downstream waste destruction zones can enhance waste destruction efficiency. In the embodiment of Figure 1 the supplemental oxidant 13 is provided to the secondary waste destruction zone 26 via addition point 23.

It is preferred that the combustion fuel 12 be natural gas, however the combustion fuel may comprise any mixture of one or more components capable of releasing heat when reacted with the oxidant. Examples of suitable combustion fuel components include but are not limited to fuel oil, hydrocarbon gases, hydrogen, flammable organics, and coal. Figure 1 illustrates the combustion fuel stream 12 being injected into the primary combustion zone 22 at a single point. However, the combustion fuel stream 12 can be added through multiple points, or it can be introduced into the primary combustion zone 22 via burners, wind boxes, mixers, distributors, injectors, nozzles, or other devices for delivering combustion fuel to combustion zone 22.

Similarly, many options may also be employed for oxidant addition to the combustion zone 22 and the waste destruction zone 26. Within the primary combustion zone 22 the oxidant stream 10 and the combustion fuel stream 12 are mixed and combusted to generate heat. In some embodiments it may be advantageous to combine the combustion fuel and oxidant prior to or concurrent with the addition to the combustion zone; common devices such as mixers, low NO_x burners (LNB), or atomizers may be employed for such purposes. The selection of appropriate fuel and oxidant addition devices is within the ability of one of ordinary skill in the art and will depend on many variables including the type of fuel and oxidant employed, thermal oxidizer geometry, and economic factors.

NO_x is generated during combustion as a result of the high temperature present in the primary combustion zone 22 and the presence of nitrogen in the oxidant stream 10 and/or the combustion fuel stream 12. The combustion process typically also produces some amount of carbon dioxide, carbon monoxide, and water.

Heat and combustion products from primary combustion zone 22 flow into the adjacent primary waste destruction zone 24 and into the secondary waste destruction zone 26. Accordingly the primary waste destruction zone 24 is termed as being “downstream” of the primary combustion zone 22 and the secondary waste destruction zone 26 is downstream of the primary waste destruction zone 24.

A waste stream 14 is introduced into the thermal oxidizer 20 via the first waste destruction zone waste stream addition point 25. The waste stream 14 generally comprises components or streams from an industrial process that are to be destroyed. The waste stream 14 can include gas, liquid, or a mixture of both and may also comprise inert components such as water, diatomic nitrogen, or carbon dioxide. The actual constituents of the waste gas stream 14 would depend on the particular industrial process under consideration, but must include at least a minimum amount of reactive waste components. By "reactive waste components" is meant waste components that are capable of reacting with oxygen that is part of a waste oxide gas molecule. Examples of such reactive waste components include but are not limited to aliphatic hydrocarbons, ammonia, acrolein, hydrogen, hydrogen cyanide, carbon monoxide, urea, and aromatics. Although such compounds may comprise oxygen atoms as part of their structure, such as carbon monoxide, compounds without oxygen are generally preferred.

It is preferred that waste streams injected into a downstream waste destruction zone comprise at least 0.5 mole% reactive waste components, or not more than 99.5 mole% inert components, to efficiently reduce WOG emissions. It is especially preferred that the waste streams comprise at least 2 mol% reactive waste components, or not more than 98 mole% inerts.

In the embodiment of Figure 1, the first waste destruction zone waste stream addition point 25 is a single connection on the outer surface of the thermal oxidizer 20, which communicates with a series of radially oriented

distribution nozzles on the inside of the thermal oxidizer 20. The nozzles provide a distributed flow about the circumference of the thermal oxidizer 20 for improved mixing and destruction efficiency. The high temperature and oxygen within the thermal oxidizer destroys the waste components.

As a result of exposure to high temperatures within the thermal oxidizer, some of the reactive waste components form radicals that are capable of removing oxygen from WOG compounds, such as NO_x, thereby converting them into inert compounds such as diatomic nitrogen and the like. Such thermally initiated radicals are herein termed "reducing radicals." Although the formation of reducing radicals should theoretically occur in any high-temperature environment, their presence is generally short lived in the primary combustion zone. As such a significant reduction in WOG emissions is not obtained.

It has been discovered that the desired result of reduced WOG emissions can be obtained when at least a portion of the reactive waste components are introduced after primary combustion occurs. This post primary combustion injection delays formation of reactive radicals and improves their efficiency in reducing WOG emissions. Accordingly, WOG emissions are effectively reduced when reactive waste components are present in a waste destruction zone downstream of the primary combustion zone.

Industrial chemical processes associated with the horizontal embodiment of the thermal oxidizer may comprise those processes producing

hydrogen cyanide, acrolein, acrylonitrile, methacrylonitrile, methacrolein, methacrylic acid, phthalic anhydride, maleic anhydride, and mixtures thereof.

It has been determined that some reactive waste components are more effective at forming thermally initiated reducing radicals at a given temperature than others, and are therefore preferred because of their greater WOG reducing capacity. Thus aliphatic hydrocarbons (e.g., hexane) would be a preferred type of reactive waste component over aromatic ring-compounds (e.g., benzene), and alkanes (e.g., propane, butane) would be preferred over alkenes (e.g., propylene, butylene) as reactive waste components.

Accordingly, industrial chemical processes which utilize alkanes rather than alkenes as their primary feed are especially preferred for use with the method of the present invention. Examples of such alkane based processes include but are not limited to production of acrolein, acrylic acid, and acrylonitrile via catalytic reaction of propane, as well as production of methacrylic acid and methacrolein from the reaction of C4-alkanes.

In the specific case of the above-cited example processes, an absorber off gas waste stream is typically generated and will comprise at least a portion of the unreacted alkane raw material feed. When such waste streams are injected into the thermal oxidizer in accordance with the method of the present invention, they can be expected to more effectively reduce NO_x than the comparable waste stream derived from the analogous alkene-based process.

It is also recognized that compounds such as CO, H₂, and NH₃ are known to be effective reducing agents and would therefore be desirable reactive waste components when utilized in accordance with the method of the present invention.

As shown in Figure 1, a portion of the waste stream 14 may also be optionally diverted at a tee 15 to provide supplemental waste stream 17. By injecting supplemental waste stream 17 into one or more of the downstream waste destruction zones, WOG emissions reduction efficiency may be enhanced. In the embodiment of Figure 1, the supplemental waste stream 17 is provided to the secondary waste destruction zone 26 via waste stream addition point 27. The addition point 27 may be comprised of a burner, wind box, mixer, distributor, injector, nozzle, or other such injection hardware.

The reactive waste components of supplemental waste stream 17 react with waste oxide gases present in the second waste destruction zone 26 that were not eliminated in the primary waste destruction zone 24. Ideally, these WOG compounds are converted within the secondary waste destruction zone 26 to compounds such as N₂, CO₂, and H₂O, which are not pollutants and can be released to the atmosphere as a harmless effluent 32. It is contemplated that in some embodiments, it may be advantageous to inject ancillary waste streams into the thermal oxidizer either through a dedicated injection point or by admixing the ancillary waste into waste stream 14 or, alternatively, supplemental waste stream 17.

Ancillary waste streams comprise waste streams that may emanate from another portion of the subject industrial process, or from a wholly different process. Such ancillary waste streams may or may not comprise significant amounts of reactive waste components and may further comprise solids, liquids, gases, or mixtures of two or more of these. Examples of such ancillary wastes include but are not limited to recovered waste fuels, organic-contaminated wastewater, process vent gases, polymer solids, or mineral acid residues. The ancillary waste streams may also comprise MMA light ends (comprising acetone, methanol, and methymethacrylate) and specialty-amine process residue (comprising t-alkyl primary amines and C6+ hydrocarbons).

In embodiments where significant liquid waste components are present in a given waste stream, such as when the waste stream comprises organic-contaminated wastewater, it is preferred that at least a portion of the liquid waste components be injected into upstream zones of the thermal oxidizer, to maximize residence time and thereby enhance waste destruction efficiency. It is especially preferred that such liquid components are at least in part injected into the primary combustion zone.

It should be noted that the dashed lines 29 represent boundaries between the various zones within the thermal oxidizer 20. The lines are dashed to indicate that exact boundaries between these zones in the thermal oxidizer are not static, but instead vary in location during a waste destruction process. Since the thermal oxidizer is a dynamic system, the boundary where primary combustion ends and waste destruction begins is not totally

stationary, but instead can move back and forth along a finite length of the thermal oxidizer 20. From a practical standpoint, the placement of a stream injection point at a distance of about 0.15 meters (0.5 feet) or more downstream of the preceding fuel or waste injection point is generally sufficient separation to maintain an independent downstream zone.

The effluent exiting the secondary waste destruction zone 26 passes into the effluent stack 30 where it is directed to the atmosphere. Optionally the effluent 32 can be directed through a heat recovery steam boiler (HRSG) 28, or other heat recovery device in order to recover some of the thermal energy contained within the effluent 32. Recovering the thermal energy of the effluent 32 improves the energy efficiency of the overall waste destruction process by recovering thermal energy from the thermal oxidizer effluent as steam.

Figure 2 represents in schematic form the preferred embodiment of the present invention where the thermal oxidizer 120 is a two-stage vertical thermal oxidizer. Vertical configurations are generally preferred over horizontal configurations for thermal oxidizers due to their reduced size and lower capital cost. In the vertical embodiment, an oxidant stream 110 and combustion fuel 112 is delivered to the primary combustion zone 122 of the thermal oxidizer 120 where the contents of the oxidant stream 110 and combustion fuel stream 112 are combusted. Thermal NO_x and other waste oxide gases are produced during combustion within the primary combustion zone 122.

The oxidant stream 110 contains one or more gases and comprises from 1 to 100% oxygen. Examples of suitable oxidants include but are not limited to atmospheric air, pure 100% oxygen, oxygen-enriched air, ozone, or oxygen-containing process vent gases. In some embodiments, rather than providing a mixed oxidant stream, it may be advantageous to utilize two independent oxidant streams which are introduced into the thermal oxidizer separately but within sufficiently close proximity to promote good mixing once inside the thermal oxidizer. For example, for safety and operability reasons, an atmospheric air stream may be injected via a nozzle separate from, but in close proximity to, a pure-oxygen addition lance.

It is preferred that the combustion fuel 112 be natural gas, however the combustion fuel may comprise any mixture of one or more components capable of releasing heat when reacted with the oxidant. Examples of suitable combustion fuel components include but are not limited to fuel oil, hydrocarbon gases, hydrogen, flammable organics, and coal. Figure 2 illustrates the combustion fuel stream 112 being injected into the primary combustion zone 122 at a single point. However, the combustion fuel stream 112 can be added through multiple points, or it can be introduced into the primary combustion zone 122 via burners, wind boxes, mixers, distributors, injectors, nozzles, or other devices for delivering combustion fuel to the primary combustion zone 122.

Similarly, many options may also be employed for oxidant addition to the primary combustion zone 122 and waste destruction zone 124. Within the

primary combustion zone 122 the oxidant stream 110 and the combustion fuel stream 112 are mixed and combusted to generate heat. In some embodiments, it may be advantageous to combine the combustion fuel and oxidant prior to or concurrent with addition to the combustion zone; common devices such as mixers, low NO_x burners (LNB), or atomizers may be employed for such purposes. The selection of appropriate fuel and oxidant addition devices is within the ability of one of ordinary skill in the art and will depend on many variables including the type of fuel and oxidant employed, thermal oxidizer geometry, and economic factors.

Another advantage of the vertical configuration of the thermal oxidizer 120 is that combustion is simplified of optional non-gaseous components, such as liquid combustion fuels and solid wastes. In a horizontal thermal oxidizer complete combustion of liquid components is dependent on the thermal oxidizer in the form of uniform small-diameter droplets that can rapidly vaporize and mix within the combustion zone. Typically, such droplets are formed using devices such as pressurized atomizers. Failure to properly operate these injection devices can lead to damaging liquid accumulations at the bottom of the horizontal thermal oxidizer, requiring costly repairs and downtime. When a vertical thermal oxidizer configuration is employed sensitivity to atomization variables is greatly reduced and liquid droplets have available the full length of the in thermal oxidizer to achieve complete combustion.

Utilization of a vertical thermal oxidizer over a horizontal one provides yet additional advantages. Vertical thermal oxidizers require less square footage to install, which is important in certain facilities. Available space for capital expansion within an existing industrial facility is often limited and sometimes not available. Thus a distinct advantage exists for processes that implement equipment having a smaller amount of required space. Due in part to the lowered space requirement, vertical thermal oxidizers can be located closer to the operating hardware of the associated industrial process. The piping connecting the process to the thermal oxidizer generally has a large diameter, often well in excess of 30 inches. Not only does situating the thermal oxidizer closer to the process eliminate the capital cost of many linear feet of expensive large diameter pipe, it also reduces the pressure drop experienced within the connecting pipe. This in turn allows the industrial process to operate at a lower pressure; which in some cases can increase product yield efficiency thereby increasing total product output.

The vertical thermal oxidizer embodiment illustrated in Figure 2 also includes optional aqueous waste stream 102. In this embodiment, aqueous waste stream 102 is injected into combustion zone 122 and comprises water and at least one additional waste compound, such as acetic acid, cyanide, inorganic salts, benzene, toluene, MIBK, etc. Alternatively, aqueous waste stream 102 could further include one or more waste streams (ancillary wastes) that emanate from another portion of the subject industrial process, or from a

wholly different process. While it is preferred that the aqueous waste stream 102 be a liquid, it could be a gas, or a mixture of gas and liquid.

The aqueous waste stream 102 could further include one or more waste streams (ancillary aqueous wastes) that emanate from another portion of the subject industrial process, or from a wholly different process. Examples of such streams include, but are not limited to light ends waste from an ethyl acrylate process (comprising ethyl acrylate, ethyl acetate and water) and waste ester distillate from a methacrylate esters process (comprising methylmethacrylate, methanol, and water).

In some embodiments, it may be advantageous to mix the aqueous waste stream with oxidant 110 or fuel 112 prior to injection into combustion zone 122. It will also be apparent to one of ordinary skill in the art that it may be possible to reduce combustion fuel demand in the thermal oxidizer if the optional aqueous waste stream 102 has a positive net heating value.

The waste stream 114 and the supplemental oxidant stream 117 are combined into the waste destruction zone inlet line 118, which then connects to one or more waste destruction zone injection points 127. The supplemental oxidant stream 117 may have the same composition as oxidant 110 or may have higher or lower oxygen content. In some embodiments, the oxidant stream 110 may comprise atmospheric air and the supplemental oxidant stream 117 may comprise oxygen containing process vent gases. Through the injection points 127 the waste oxidant stream of inlet line 118 is injected into the waste destruction zone 124 of the thermal oxidizer 120.

The injection points 127 may be radially oriented along the exterior of the thermal oxidizer 120 adjacent the waste destruction zone 124 or arranged in some other configuration which promotes uniform mixing within the waste destruction zone. Each injection point 127 provides a premixed supply of the waste stream 114 and the supplemental oxidant stream 117. Premixing the waste stream 114 and the supplemental oxidant stream 117 enhances destruction efficiency and also reduces the required number of injection ports.

Fewer injection ports reduce the required size of waste destruction zone 124 and the overall size and cost of the thermal oxidizer 120. It is contemplated that under some circumstances it may be advantageous to inject the supplemental oxidant stream 117 and the waste stream 114 independently into the waste destruction zone 124, or possibly omit use of the supplemental oxidant stream 117 altogether.

The waste stream 114 generally comprises components or streams from an industrial process that are to be destroyed. The waste stream 114 can include gas, liquid, or a mixture of both and may also comprise inert components such as water, diatomic nitrogen, or carbon dioxide. The actual constituents of the waste gas stream 14 would depend on the particular industrial process under consideration, but must include at least a minimum amount of reactive waste components. Examples of such reactive waste components include but are not limited to aliphatic hydrocarbons, ammonia, acrolein, hydrogen, hydrogen cyanide, carbon monoxide, urea, and aromatics. Although such compounds may comprise oxygen atoms as part of their

structure, such as carbon monoxide, compounds without oxygen are generally preferred. It is preferred that waste streams injected into a downstream waste destruction zone comprise at least 0.5 mol% reactive waste components, or not more than 99.5 mol% inert components, to efficiently reduce WOG emissions. It is especially preferred that the waste streams comprise at least 2 mol% reactive waste components, or not more than 98 mol% inert components. Industrial chemical processes associated with the vertical embodiment of the thermal oxidizer may comprise those processes producing hydrogen cyanide, acrolein, acrylic acid, acrylonitrile, methacrylonitrile, methacrolein, methacrylic acid, phthalic anhydride, maleic anhydride, and mixtures thereof.

It is contemplated that in some embodiments, it may be advantageous to inject ancillary waste streams into the thermal oxidizer 120 either through a dedicated injection point or by admixing the ancillary waste into waste stream 114 or, alternatively, supplemental waste stream 117. Ancillary waste streams comprise waste streams that may emanate from another portion of the subject industrial process or from a wholly different process. Such ancillary waste streams may or may not comprise significant amounts of reactive waste components and may further comprise solids, liquids, gases, or mixtures of two or more of these. Examples of such ancillary wastes include, but are not limited to, recovered waste fuels, organic-contaminated wastewater, process vent gases, polymer solids, or mineral acid residues.

In embodiments where significant liquid waste components are present in a given waste stream, such as when the waste stream comprises organic contaminated wastewater, it is preferred that at least a portion of the liquid waste components are injected into upstream zones of the thermal oxidizer. This upstream injection maximizes residence time and thereby enhances destruction efficiency. It is especially preferred that a portion of such liquid components are injected into the primary combustion zone.

As previously described with respect to the horizontal thermal oxidizer 20, at least a portion of the reactive waste components injected into the vertical thermal oxidizer 120 are converted into reducing radicals within the waste destruction zone 124. The reducing radicals thereafter react with the waste oxide gases present in the waste destruction zone to reduce WOG emissions from the waste destruction process. The effluent exiting the waste destruction zone 124 passes into the effluent stack 130 where it is directed to the atmosphere. Optionally, prior to entering the effluent stack 130, the effluent 132 can be directed through a heat recovery steam boiler (HRSG) 128, or other heat recovery device in order to recover some of the thermal energy contained within the effluent 132. Recovering the thermal energy of the effluent 132 improves the energy efficiency of the overall waste destruction process by recovering thermal energy from the thermal oxidizer effluent as steam.

EXAMPLES

Referring now to the process configuration of Figure 1, an example is provided illustrating the improved and novel features of a specific embodiment of the present invention. This specific embodiment relates to an acrylic acid production process.

For illustrative purposes, the operation of the thermal oxidizer 20 represented in Figure 1 will be described with respect to its application to an industrial chemical process for making acrylic acid via catalytic oxidation of propylene. However, the method of invention may be employed with other industrial processes and the following example is not intended to limit the scope of the invention in any way.

EXAMPLE 1

In an industrial chemical process for making acrylic acid from propylene feed, a horizontal three stage thermal oxidizer of the type illustrated in Figure 1 was employed to dispose of waste streams. The furnace section of the thermal oxidizer (from addition point 21 to the end of waste destruction zone 26) was approximately 15.9 meters (52 feet) long. The inside diameter of primary waste destruction zone 24 was 1.8 meters (6 feet) and the inside diameter of secondary waste destruction zone 26 was 3.2 meters (10.5 feet). The base load NO_x emissions for the thermal oxidizer were determined as follows:

Natural Gas from a commercial pipeline was used as the combustion fuel stream 12 and was injected into the primary combustion zone at a rate of

24, 525 liters/minute (866 scfm). Ambient temperature atmospheric air was used for oxidant stream 10. The airflow was injected into the primary combustion zone 22 at a rate of 310,387 liters/minute (10,960 scfm) and into the secondary waste destruction zone 26 at a rate of 310,387 liters/minute (10,960 scfm). The firebox temperature averaged 818° C (1505 ° F) and the stack 33 oxygen level (as measured on a wet basis) was 13 mol%. No waste stream was supplied to the incinerator (stream 14 flow rate was zero) and the base-load NO_x emission rate was determined to be 1.51×10^{-04} mg NO_x /cal (0.084 lb NO_x/MM BTU) fired.

COMPARATIVE EXAMPLE 1

In the same industrial chemical process for making acrylic acid from propylene feed and employing the same horizontal three stage thermal oxidizer as in Example 1, the operation of the thermal oxidizer was adjusted in accordance with the method of the present invention to achieve reduced NO_x emissions. The specific operation was as follows:

Natural Gas from a commercial pipeline was used as the combustion fuel stream 12 and was injected into the primary combustion zone at a rate of 36,306 liters/minute (1282 scfm). Ambient temperature atmospheric air was used for the oxidant stream 10 and was injected into the primary combustion zone 22 at a rate of 646,262 liters/minute (22,820 scfm) and into the secondary waste destruction zone 26 at a rate of 431,030 liters/minute (15,220 scfm). The firebox temperature averaged 862° C (1583° F) and the stack 30 oxygen level (as measured on a wet basis) was 3 mol%. A 60° C (140° F), gaseous waste

stream 14 comprising 98 mole% inerts (e.g., nitrogen, water, carbon dioxide, oxygen, and argon), 0.9 mole% aliphatic hydrocarbons (e.g., propylene, propane), and 1.1 mole% other reactive waste components (e.g., carbon monoxide, acetic acid, acrolein, etc.) were provided to the incinerator, yielding a total reactive waste component feed concentration of 2 mole%. The waste stream 14 was split into two portions at tee 15: the first portion was injected through a twelve-hole circumferential distributor at a rate of 658,723 liters/minute (23,260 scfm) into the primary waste destruction zone (at point 25, located approximately 0.76 meters (2.5 feet) downstream of oxidant injection point 21); the second portion was injected through a thirty-hole circumferential distributor at a rate of 329,362 liters/minute (11,630 scfm) into the secondary waste destruction zone (at point 31, located approximately 0.76 meters (2.5 feet) downstream of waste stream injection point 21). The resulting NO_x emission rate was determined to be 7.2×10^{-05} mg NO_x/cal (0.040 lb NO_x/MM BTU) fired, representing a NO_x emissions reduction of over 50% as compared to the base-load case of Example 1. Thus the method of the present invention can be seen to provide a significant reduction in WOG emissions from the waste destruction process.

The present invention described herein, therefore, is well adapted to carry out the objects and attain the ends and advantages mentioned, as well as others inherent therein. While several presently preferred embodiments of the invention have been given for purposes of disclosure, numerous changes in the details of procedures may be made for accomplishing the desired

results. For example, the present invention can involve handling any industrial process waste stream that includes waste destruction as a part of the process. Further, it will be evident that the invention is particularly well suited to treat the industrial chemical process waste streams, such as those produced in the manufacture of (meth)acrolein, hydrogen cyanide, (meth)acrylonitrile, (meth)acrylic acid, phthalic anhydride, maleic anhydride, and other similar products. Additionally, it is envisioned that in some embodiments, it may be beneficial to combine prior-art WOG emissions reduction technologies, such as low NO_x burners and Selective Catalytic Reduction systems, with the method of the present invention. These and other similar modifications will readily suggest themselves to those skilled in the art, and are intended to be encompassed within the spirit of the present invention disclosed herein and the scope of the appended claims.